Temporal decrease in upper atmospheric chlorine

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Abstract

We report a steady decrease in the upper stratospheric and lower mesospheric abundances of hydrogen chloride (HCl) from August, 2004, through January, 2006, as measured by the Microwave Limb Sounder (MLS) aboard the Aura satellite. For 60°S to 60°N zonal means, the average yearly change in the 0.7 to 0.1 hPa (~50 to 65 km) region is –27 ± 3 pptv/year, or –0.78 ± 0.08 percent/year. This is consistent with surface abundance decrease rates (about 6 to 7 years earlier) in chlorine source gases. The MLS data confirm that international agreements to reduce global emissions of ozone-depleting industrial gases are leading to global decreases in the total gaseous chlorine burden. Tracking stratospheric HCl variations on a seasonal basis is now possible with MLS data. Inferred stratospheric total chlorine (Cl_{TOT}) has a value of 3.60 ppbv at the beginning of 2006, with a (2-sigma) accuracy estimate of 7%; the stratospheric chlorine loading has decreased by about 43 pptv in the 18-month period studied here. We discuss the MLS HCl measurements in the context of other satellite-based HCl data, as well as expectations from surface chlorine data. A mean age of air of ~ 5.5 years and an age spectrum width of 2 years or less provide a fairly good fit to the ensemble of measurements.

1. Introduction

The abundances of chlorine and bromine gases in the Earth's stratosphere have garnered much attention in ozone depletion assessments [e.g., *WMO*, 2003], because of the consensus regarding the importance of industrially-produced source gases such as chlorofluorocarbons (CFCs) and halons. Measurements from surface networks, as well as from aircraft, have produced a record of chlorine gases and their total abundance (Cl_{TOT}) in the troposphere for more than two decades. Also, ground-based column measurements of (largely stratospheric) hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$), as well as satellite-based near-global observations of HCl at high altitude (near 55 km), have documented the long-term increase in total stratospheric chlorine up until the late 1990s, with indications of a turn-around in recent years [*Anderson et al.*, 2000; *WMO*, 2003; *Mahieu et al.*, 2004]. The vast majority of chlorine in the upper stratosphere and lower mesosphere is present as HCl, as shown by early observations from the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment [*Zander et al.*, 1996], and recently corroborated by data from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS, often simply referred to as ACE, below) aboard the Canadian satellite SCISAT-1 [*Bernath et al.*, 2005].

Here, we report and analyze recent decreases in upper atmospheric HCl, observed by the Earth Observing System (EOS) Microwave Limb Sounder (MLS) aboard the Aura satellite, launched July 15, 2004. These results are discussed in the context of other HCl measurements, including those from ACE and the 14-year record from the Halogen Occultation Experiment (HALOE) [*Russell et al.*, 1993] on the Upper Atmosphere Research Satellite (UARS). We discuss the implications of the various results in terms of stratospheric total chlorine and decreases expected from tropospheric chlorine data.

1   **2. Variations in tropospheric chlorine and upper atmospheric MLS HCl data**

2   Figure 1 shows the tropospheric chlorine abundance based on surface

3   measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE)

4   network [e.g., *O'Doherty et al.*, 2004], and from the National Oceanic and Atmospheric

5   Administration (NOAA) network [*Montzka et al., 1999*]. The latitudinal coverage from

6   these near-global networks spans the tropics, mid- and high latitudes (from 41°S to 53°N

7   for AGAGE and from the South Pole to 82°N for NOAA). We have averaged these two

8   data sets to produce a mean value for total chlorine in the troposphere. Differences in

9   total tropospheric chlorine between the two networks are less than 30 ppt (1%) over the

10   time period of overlap, although independent measures of ~20% of the total (CH_3Cl,

11   CFC-114, and CFC-115) are not currently available. Note that parts per trillion or per

12   billion are typically used here for the units of ground-based source gas measurements

13   since those refer to a mole fraction and not a volume mixing ratio; these units are

14   compatible, however, with the units of pptv or ppbv that we use (here) for mixing ratios

15   from satellite retrievals. This chlorine loading peaked in late 1993 to early 1994 at close

16   to 3.7 ppb (the peak combined value from Figure 1 is 3.692 ppb). Peak tropospheric

17   Cl_{TOT} should represent an upper limit for stratospheric Cl_{TOT}.   The peak in the

18   stratosphere is expected a number of years later, and mixing will tend to reduce the peak

19   by an amount that is sensitive to the age of air spectrum. The total chlorine abundances

20   in Figure 1 include 100 ppt from the chlorinated very short-lived (VSL) gases CH_2Cl_2,

21   $CHCl_3$, C_2Cl_4, and $COCl_2$. The latter compound (phosgene) accounts for about half of the

22   100 ppt potential chlorine from VSL gases. It is unclear how much this compound

23   contributes to stratospheric Cl_{TOT} [*Kindler et al.*, 1995], although balloon-borne

24   measurements [*Toon et al.*, 2001] indicate ~25 pptv in the lower stratosphere, with near

25   zero values in the upper stratosphere, suggesting the full 50 ppt contribution to Cl_{TOT} may

1   be occurring. The uncertainty in the 100 ppt from VSL compounds is possibly ~50 ppt,

2   which could include compounds other than phosgene. Also, models indicate that perhaps

3   30 ppt of HCFC-22 (a long-lived source gas) is present near 55 km, for 2004 [*Nassar et*

4   *al.*, 2006]. For total chlorine contained in long-lived source gases, the root sum square

5   difference between the two networks is ~23 ppt, or 0.6%. This becomes 1.8% if one adds

6   (in root sum square fashion) a 50 ppt uncertainty from VSL compounds and a 30 ppt

7   uncertainty due to HCFC-22. An accuracy of ~2% therefore seems to represent the state

8   of knowledge for the total tropospheric chlorine burden converted to inorganic chlorine in

9   the upper stratosphere.

10   MLS, one of 4 instruments aboard Aura, measures thermal emission from the

11   limb in five spectrally-broad regions [*Waters et al.*, 2006]. HCl emission lines near 625

12   GHz are used to retrieve ~3500 HCl profiles daily (day and night) with ~165 km spacing

13   along the 82°S to 82°N sub-orbital track. Vertical resolution for HCl data (version 1.51)

14   is ~3-4 km in the lower stratosphere and 6 km in the upper stratosphere. The MLS

15   retrievals [*Livesey et al.*, 2006] use a linearly-connected set of coefficients on a 6-point

16   per decade pressure grid and account for horizontal variations along the sub-orbital track.

17   MLS sensitivity to HCl is evident in the MLS radiance data as high as the upper

18   mesosphere. Early validation of HCl from MLS with other satellite and balloon data is

19   described by *Froidevaux et al.* [2006], with further discussion in section 3. A detailed

20   discussion of the estimated uncertainties (random and systematic) in upper stratospheric

21   MLS HCl is given in the auxiliary material (Appendix A).

22   Figure 2 shows that MLS has measured a decrease in HCl abundances in the

23   upper stratosphere and lower mesosphere between August 2004 and January 2006. The

24   MLS measurement density, repeatability, and precision allow global HCl decreases on a

25   seasonal basis to be precisely tracked (within a given year) for the first time. The average

1   yearly decrease, based on an average of the first 6 months and the last 6 months of these

2   time series, amounts to about 27 pptv (with a scatter from the various altitudes of 3 pptv),

3   or a slope of –0.78 %/yr (and scatter of 0.08 %/yr). The HCl changes shown in Figure 2

4   are well outside the typical precision in the monthly means; for example, the 2-sigma

5   uncertainty at 0.46 hPa (~53 km) is under 0.003 ppbv, and ~20 times less than the total

6   change. Tropospheric chlorine variations, with a time lag, should govern the overall

7   temporal changes in upper stratospheric and lower mesospheric total chlorine, although

8   some non-linear effects due to mixing can occur [e.g., *Waugh et al.*, 2001]. A calculation

9   of decrease/year as performed for the MLS HCl data, but based on tropospheric chlorine

10   variations time-lagged by 7 years and multiplied by 0.96 to account for the ratio

11   HCl/Cl_{TOT}, gives 29 pptv/year, in very good agreement with MLS data. The factor of

12   0.96 is based on the 2-D Simulation of Chemistry, Radiation, and Transport of

13   Environmentally important Species (SOCRATES) model results shown in Figure 3, as

14   well as recent evidence from an ACE-FTS inventory of chlorine species in the

15   stratosphere [*Nassar et al.*, 2006], indicating slightly larger ratios (0.96 to 0.98) for

16   HCl/Cl_{TOT} in the upper stratosphere. Peak values of HCl/Cl_{TOT} shown in Figure 3 are

17   between 0.95 and 0.96; additional model chlorine above 55 km comes mainly from ClO

18   and Cl (~ 3% of total), from the $CHClF_2$ (HCFC-22) long-lived organic contribution (~

19   1%), and HOCl (0.5%). A time lag of 6 years also leads to reasonable agreement

20   between the MLS data in Figure 2 and expectation, the ground-based decrease (6 years

21   earlier) being ~27 pptv/year. However, a lag under 5 years produces a decrease of under

22   20 pptv/year, which is less consistent with MLS data. The smaller decrease (for shorter

23   time lags) occurs because the rate of decline of tropospheric chlorine has slowed in recent

24   years, mainly as a result of the rapid but (now) slowing decline in CH_3CCl_3 [*Montzka et*

25   *al.*, 1999; *O'Doherty et al.*, 2004].   More complex (and probably more robust)

1   considerations of time lags, involving mean age (transport timescale) of air and spectral

2   widths of the age distribution for a mixture of air parcels are discussed in section 3.

3   Figure 4 shows global upper atmospheric averages of MLS HCl and inferred

4   values of Cl_{TOT} versus height, with the conversion of HCl to Cl_{TOT} based on an

5   integration of SOCRATES 2-D model HCl/Cl_{TOT} values in ten degree latitude bins. The

6   differences between August 2004 and January 2006 show that the temporal decrease has

7   occurred at all heights in this region. Cl_{TOT} (averaged over the various pressures) has

8   changed from 3646 to 3603 pptv in this 18-month period, for an average decrease of

9   43 pptv ± 9 pptv (precision in the mean). Cl_{TOT} is fairly constant with height, meaning

10   that model and MLS HCl dependences on height are quite similar; the Cl_{TOT} values near

11   the peak are less sensitive to the model profile shape. At the highest altitudes, both MLS

12   and model values show a small decrease attributed to photolysis of HCl. The 2-sigma

13   accuracy estimate for MLS HCl is ~ 5%, based on a consideration of the various possible

14   error sources, as discussed in detail in the auxiliary material (Appendix A); uncertainties

15   arising from HCl linewidth parameters account for more than half of this value. The

16   estimated accuracy for inferred Cl_{TOT} is 7%, obtained by (conservatively) adding 2%

17   uncertainty from HCl/Cl_{TOT}.

18   **3. Other Results and Discussion**

19   The average rate of HCl decline (about -0.8%/yr) observed by MLS is

20   commensurate with ground-based expectations from total tropospheric loading and also

21   with the -0.7%/yr rate of change in total inorganic chlorine observed since 1997 above

22   the Swiss Alps, based on infrared column measurements of HCl and $ClONO_2$ [*Mahieu et*

23   *al.,* 2004]. Also, there is evidence for a decrease in upper stratospheric ClO since about

24   1994, from analyses of ground-based microwave data from Hawaii by *Solomon et al.*

1 [2006], who obtained a ClO rate of change near 4 hPa of roughly -1.5%/yr from 1994

2 through 2004, with possibly one third of this caused by changes in methane.

3   To place the MLS measurements in the context of other satellite data sets for HCl,

4 Figure 5 shows the MLS monthly mean HCl time series at 0.46 hPa for 60°S – 60°N,

5 similarly-averaged HALOE (version 19) monthly means (interpolated to 0.46 hPa), and

6 ACE (version 2.2) data at 53.5 km (~ 0.49 hPa) averaged in nine 3-month periods

7 (quarterly, from January, 2004, through March, 2006). We also show version 3 data

8 [*Irion et al.*, 2002] from the four ATMOS missions, using HCl retrieval averages from 50

9 to 60 km in the above latitude range; the ATMOS data contain the fewest profiles and

10 averaging over height helps to reduce the noise to below the accuracy estimate. ACE

11 HCl values in the upper stratosphere are, on average, a few to 5% larger than MLS data,

12 and are larger than HALOE HCl by 10-15% or more; however, ACE HCl in the lower

13 mesosphere departs more from (and is progressively larger than) MLS HCl, as altitude

14 increases [*Froidevaux et al.*, 2006; *Nassar et al.*, 2006]. More work will be needed to

15 decide whether ACE HCl values are too high in the mesosphere. The average ACE HCl

16 abundance (near 53 km) from Figure 5 is 3.69 ppbv, with (1-sigma) variability of

17 ~0.2 ppbv. However, ACE provides a mean 2004 Cl_{TOT} estimate at lower altitudes of

18 ~3.65 ppbv [*Nassar et al.*, 2006], which is more consistent with the MLS measurements

19 of HCl above 50 km, and in excellent agreement with the August 2004 MLS Cl_{TOT}

20 estimate (also 3.65 ppbv, from Figure 4). We use a 2-sigma accuracy for ACE HCl of

21 0.3 ppbv, slightly larger than twice the 1-sigma estimate of 0.13 ppbv given by *Nassar et*

22 *al.* [2006] for midlatitude HCl at 50 km. The main error sources mentioned in the latter

23 work are line intensity (0.08 ppbv), retrieved temperature and pressure (0.08 ppbv), and

24 closure of the spectral fits (0.06 ppbv). The value of 0.3 ppbv as an error bar is used for

25 ATMOS data also, consistent with ATMOS HCl error estimates [e.g., *Zander et al.*,

26 1996]. One could draw a time series consistent with all results within their uncertainties

1   (including the HALOE 13% accuracy); this would require an adjustment of HALOE

2   HCl upward and ATMOS, ACE, and (possibly) MLS data downward by varying

3   amounts.

4   In Figure 5, the HCl data sets are compared to expectations of long-term

5   variations in HCl, as obtained from tropospheric chlorine estimates and considerations of

6   mean age of air and various age spectrum widths [e.g., *Waugh and Hall*, 2002] relating to

7   transport timescales and irreversible mixing of air parcels moving from the surface to the

8   upper stratosphere. The tropospheric chlorine burden is based on total chlorine loading

9   from Figure 1 as well as an example for the WMO 2002 Ab scenario [*WMO*, 2003],

10   which peaks at 3.58 ppbv instead of 3.69 ppbv, because it only includes contributions

11   from the 12 most abundant long-lived halocarbons. If VSL compounds are transported

12   across the tropopause, it is likely that their decomposition products will contribute to

13   upper stratospheric Cl_{TOT}. However, questions remain regarding how much chlorine can

14   reach the lower stratosphere, either by cross-tropopause transport of the VSL species or

15   of their decomposition products [*WMO*, 2003]. The satellite results do not place strong

16   constraints on possible chlorine contributions from VSL gases, because of the absolute

17   uncertainties in the measurements and differences between the data sets. While HALOE

18   data are most consistent with no chlorine contribution from VSL compounds, the MLS,

19   ACE, and ATMOS data suggest a significant contribution.

20   Multi-year balloon-borne observations of stratospheric tracers such as CO_2 and

21   SF_6 have led to a mean age estimate of ~5.5 years in the middle stratosphere [*Schmidt*

22   *and Khedim*, 1991; *Engel et al.,* 2002], but this is not constrained to better than ~1 year.

23   Age of air is probably roughly constant in the upper stratosphere, given that these and

24   other balloon CO_2 measurements exhibit very weak vertical gradients above 25-30 km.

25   MLS data alone cannot distinguish between mean ages of 5.5 or 7 years, shown as

26   examples in Figure 5, or even 4 years (not shown), although closer agreement with the

1   data is obtained for 7 years. While a better constraint on mean age could be obtained

2   from HCl during the phase of rising chlorine, the error bars and differences between data

3   sets preclude a useful constraint. The ATMOS data would be more consistent with an

4   age of 4 to 5 years, while HALOE data favor a value larger than ~5.5 years. A mean age

5   of ~5.5 years (consistent with results from balloon-borne data) might best accommodate

6   the ensemble of data sets, within their uncertainties. The decrease implied by MLS data

7   favors a width of the age spectrum of 2 years or less.

8   HALOE data since 2000 show a steeper decrease (by a factor of two or more)

9   than MLS and the various model curves, and explaining some of the variations obtained

10   by HALOE has proved difficult [*Waugh et al.*, 2001]. The scatter in MLS monthly

11   means using a subset of data with a sampling that mimics the HALOE occultation data

12   coverage was found to be smaller than the scatter in HALOE means, but larger than when

13   using the full MLS sampling. ACE seasonal averages in Figures 5 also show more

14   variability than the MLS data, while not being inconsistent with expected decreases.

15   Also, the HALOE data appear to vary coherently over at least a 5 to 6 km range (for

16   altitudes near those used and shown here). This range corresponds to the vertical

17   resolution of MLS in that region, so the coarser MLS resolution should not significantly

18   mask variations such as those exhibited in the HALOE data set; a smoothing of the

19   temporal decrease would not be an expected result either. Thus, poorer (and less

20   repeatable) sampling in the occultation data sets is partly responsible for explaining the

21   larger variability of the HCl time series, even if that is not the only factor. Other factors

22   could include unknown or poorly characterized error sources leading to more (temporal)

23   variability than expected in HALOE averages or to less variability in the MLS results.

24   The MLS upper atmospheric HCl measurements to date imply that international

25   agreements to reduce global emissions of ozone-depleting industrial gases are leading to

26   global decreases in stratospheric chlorine, consistent with the observed decrease in

1   surface chlorine burden. Several more years of data will better constrain our

2   knowledge of stratospheric age of air spectrum width and transport-related variability.

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6   **Acknowledgements**

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1   **Figure 1.** Tropospheric total chlorine based on source gas network data at the Earth's

2   surface from AGAGE (green) and NOAA (blue). An average curve based on the

3   overlap time period is shown in red. Insert gives the difference (NOAA - AGAGE).

4   **Figure 2.** Monthly-averaged MLS HCl zonal means (curves with dots) over 60°S to

5   60°N for Aug. 2004 through Jan. 2006, at 6 upper atmospheric pressures, as indicated

6   by colored labels. Dashed black lines show the uncertainty due to imprecision at 0.46

7   hPa, defined here as ± twice the standard error in the mean. Purple curve is upper

8   atmospheric HCl expected from tropospheric chlorine loading (average from Figure 1),

9   time-shifted by 7 years and adjusted by 0.96 for the HCl/Cl_{TOT} ratio (near 0.46 hPa).

10   **Figure 3.** Upper stratospheric and lower mesospheric HCl/Cl_{TOT} ratios based on recent

11   NCAR SOCRATES 2-D model results at various northern latitudes (see legend).

12   Values correspond to steady-state averages (3-year integration), after a model spin-up of

13   seven years. Similar values are obtained for southern latitudes (not shown).

14   **Figure 4.** Global average upper stratospheric and lower mesospheric MLS HCl (dots)

15   and inferred Cl_{TOT} (triangles) for August 2004 (red) and January 2006 (black). Cl_{TOT} is

16   inferred using SOCRATES 2-D model results for HCl/Cl_{TOT} (see Figure 3). These

17   results are based on zonal means in 10 degree latitude bins, weighted by (cosine of)

18   latitude.

19   **Figure 5.** Top panel: Solid (blue) curve shows total chlorine (Cl_{TOT}) time series based

20   on tropospheric data (Figure 1). Dashed curve does not include contributions from

21   short-lived chlorinated substances (WMO 2002 scenario Ab). Middle and bottom

22   panels: HCl data are shown as 60S-60N monthly averages at 0.46 hPa (~ 53 km) for

23   MLS (red dots), similar averages for HALOE (purple circles), along with quarterly

24   averages (at ~ 53 km) from ACE (in green) and ATMOS version 3 data averages (cyan

25   squares) for 50-60 km; see text for more discussion of data and error bars (2-sigma

estimates of accuracy). Solid curves use total chlorine (top panel's solid curve) and different mean age assumptions (5.5 or 7 yr), with various age spectrum widths, as indicated; a factor of 0.96 is applied to get HCl. The dashed black curves give expected HCl based on the WMO 2002 scenario Ab and a mean age (5.5 or 7 yr) and width (2 yr) appropriate for the solid black curves.
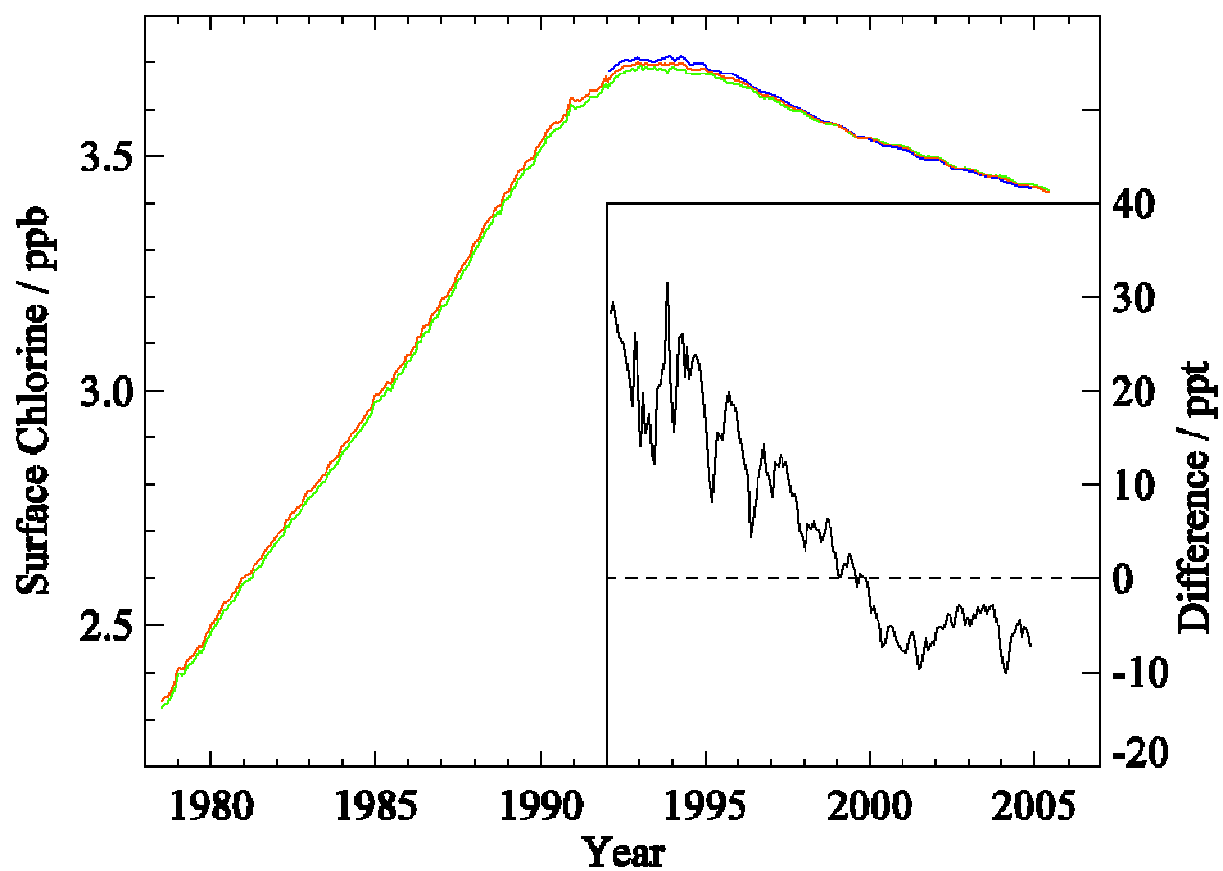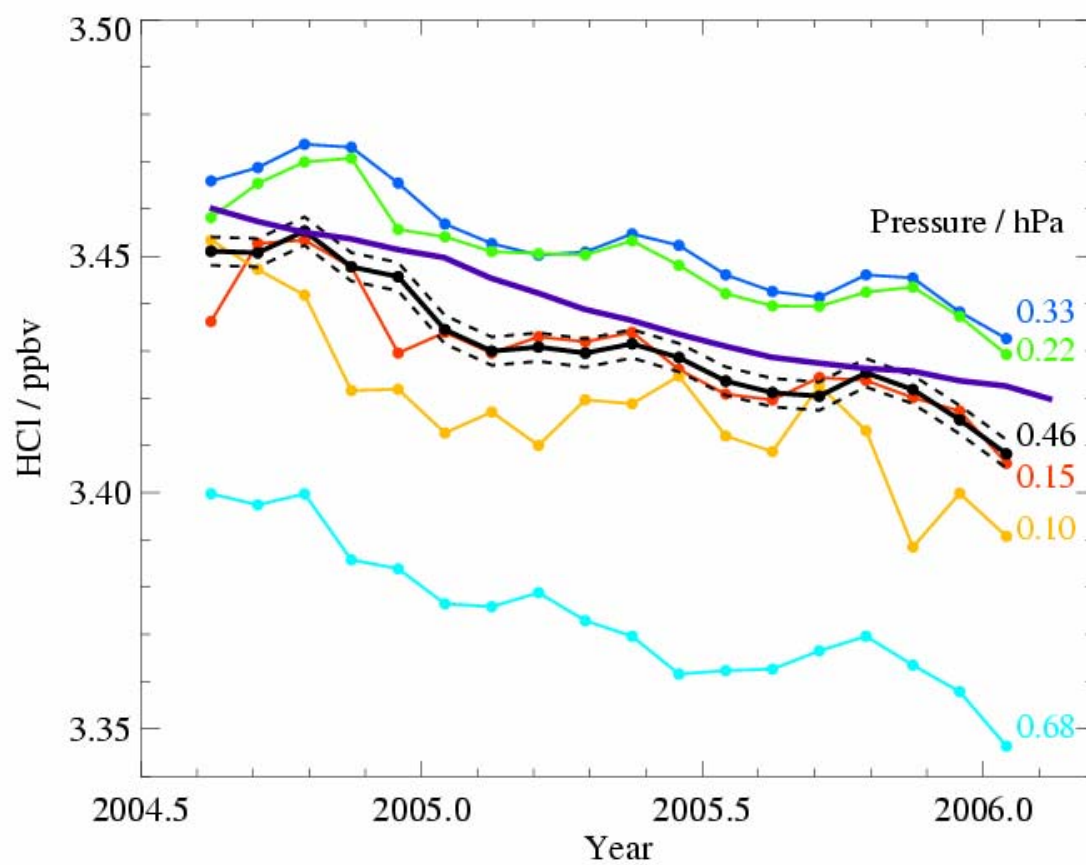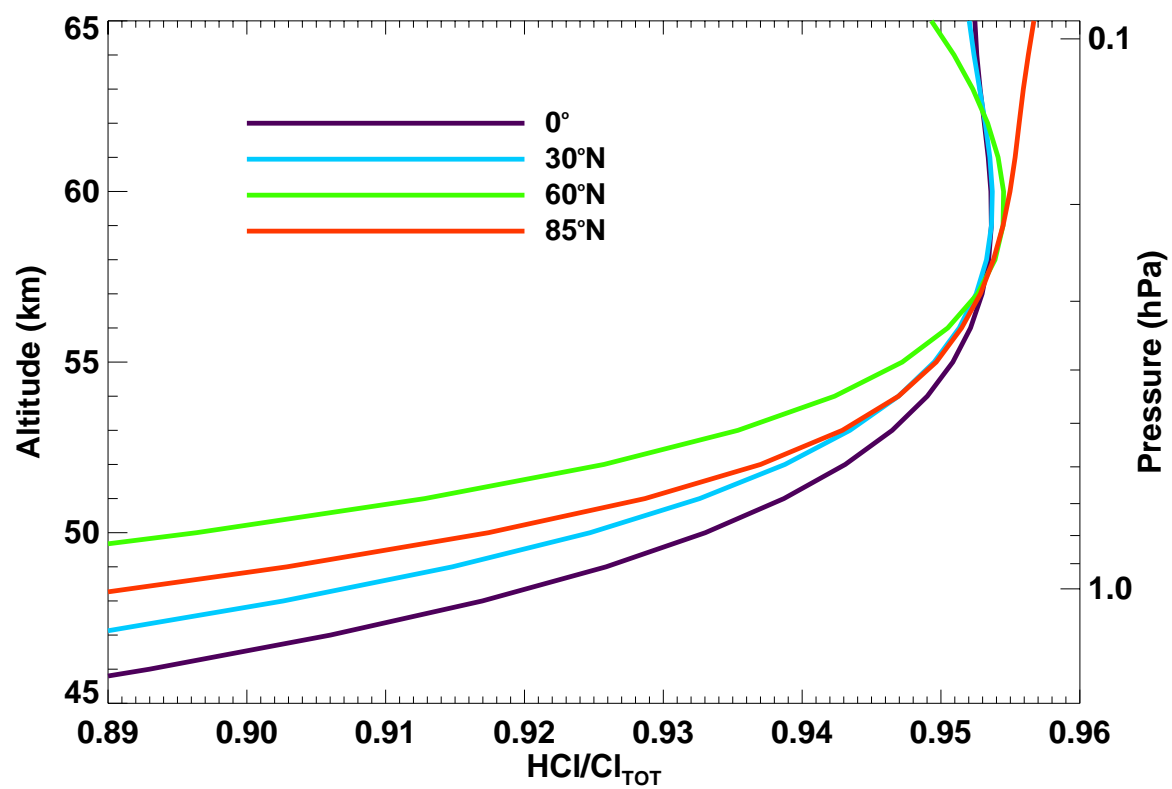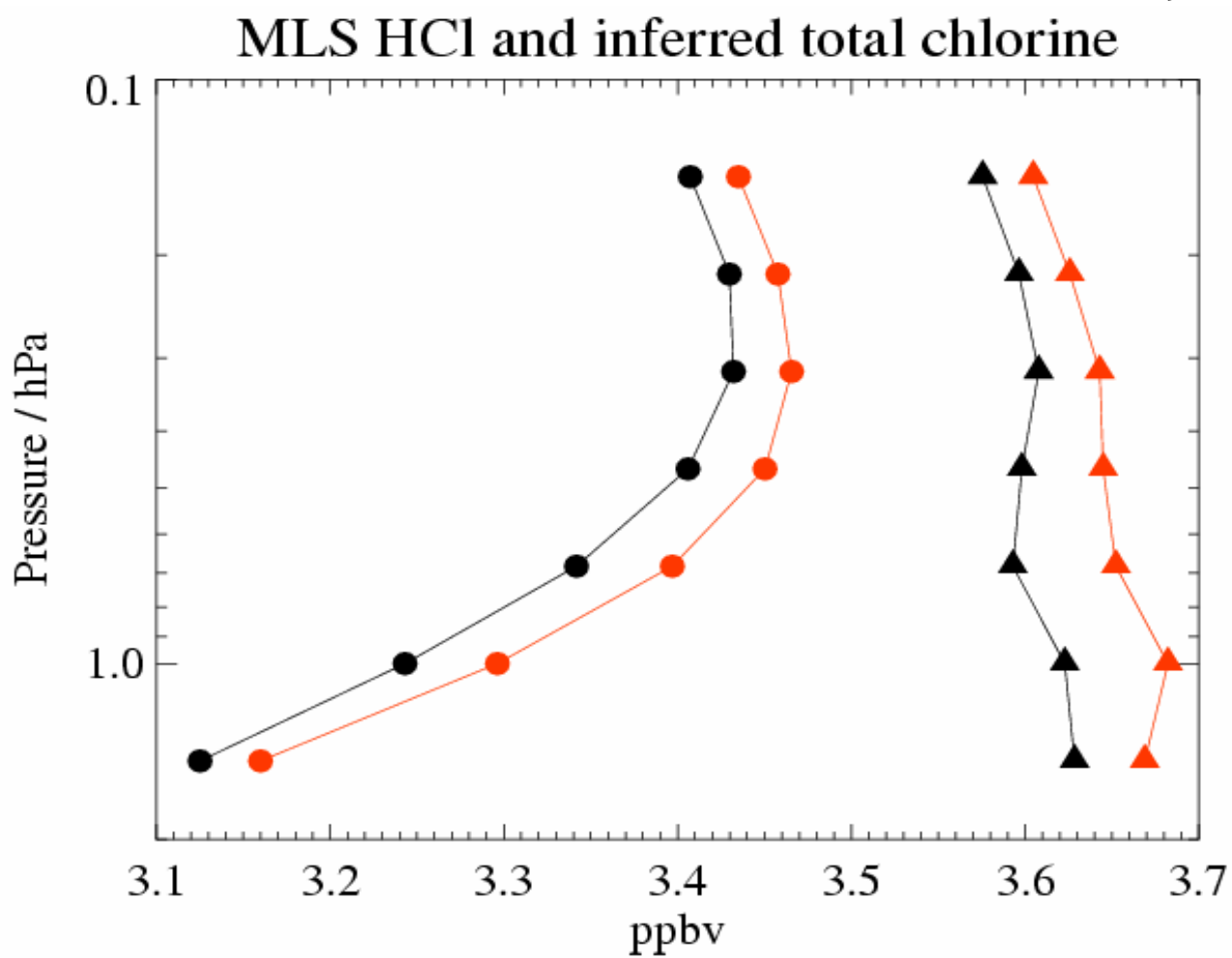
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